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ACCURATE DETERMINATION OF AUGER LINE SHAPE BINDING ENERGIES

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ACCURATE DETERMINATION OF AUGER LINE SHAPE BINDING ENERGIES

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ABSTRACT

A quantitative comparison between an experimental and a theoretical description of any Auger spectrum requires a common energy reference point such as the Fermi level. With non-conductors this is problematic, since the Fermi level is not well defined and charging may shift the Fermi level. A common approach to overcome this problem employs spectra containing the Auger peak, core, and valence band (VB) photoemission peaks. One then has only to locate a common reference point in the Auger and VB spectra relative to the core level peak. We have developed a procedure where a comparison is made between model theoretical and experimental spectra so that a large energy range (about 20 eV) of each spectrum can be utilized to locate the common reference points. We have found that this method enables accurate reference points to be determined even with severe sample charging. The method is precise enough to observe what may be a differential charging effect in the polyethylene (PE) spectra. This suggests that the photoelectron and Auger peaks may not shift an equal amount with charging in all instances, an assumption often made with the use of the Auger parameter. Although much smaller than that previously reported, a breakdown in the Cini-Sawatzky expression as modified for covalent systems still is suggested for PE. This breakdown can now be attributed to the limited one-dimensional delocalization required in long chain polymers.

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INTRODUCTION

Auger Electron Spectroscopy (AES) is widely used for qualitative elemental analysis of solid surfaces and in depth profiles. Identification of the chemical state of the detected element often can be made by a "finger print" approach, e.g., various forms of carbon (1,2) or S^{2-} and SO_4^{2-} (3) are easily recognized in this manner. In other cases, information about the chemical state can be determined from the relative peak energies or chemical shifts, e.g., Si vs. SiO_2 (4). When the Auger spectra are obtained with an X-ray source, chemical state identification can be made with the use of the Auger parameter (5). Utilization of the Auger parameter requires measurement of the energy difference between the main photoelectron and Auger transitions. None of these approaches require knowledge of the absolute energy scale, since only line shape changes or shifts are required. Indeed, an advantage of the Auger parameter is that it is not necessary to know the absolute energies of the peaks being used.

However, AES has the potential to provide much more information; for example, the nature of the bonding, the character of the screening response to creation of a core hole, and the magnitude of the electron correlation (6). A measure of the latter can be obtained from the hole-hole repulsion energy (7) defined from the equation,

$$E_A(cvv) = E_A(c) - E_A(v) - E_A(v') - U(vv') \quad (1)$$

where c refers to the core level, v is the valence level, and $U(vv')$ is the final state hole-hole repulsion energy.

In a large covalent molecule such as PE, the number of valence orbital combinations vv' is huge, so that estimates of the average value of $U(vv')$ ($=\bar{U}$) are often made from the shift of the dominant peak in the Auger line shape (6). In a method to be described below, Rye (8) obtained estimates of U (VBM VBM) where VBM is the highest occupied molecular orbital (HOMO) or valence band maximum. On the other hand, within the Cini-Sawatzky theory (9-11) normally used to interpret Auger line shapes of extended covalent or metallic systems, two repulsion parameters, ΔU and U_0 enter (see appendix). It is necessary to carefully relate these different U parameters.

The ΔU parameter, which we call the correlation parameter, determines the extent of the line shape distortions. With increasing ΔU , the distortion increases. If ΔU is greater than some valence band width, the Auger peak will be atomic-like, i.e., sharp and shifted downward in energy. Conversely, if ΔU is less than the band width, the Auger peak will have a band-like line shape (9-11), i.e., small line shape changes. In studies of graphite, diamond, PE, and a series of alkanes and alkenes (12,13), we have found that $\Delta U \approx U_{II}-U_{II}$ can be thought of as the difference between the hole-hole repulsion when both holes are localized on the same sp^3 like methyl group versus when they are on neighboring methyl groups. In the alkanes, including PE, the ΔU parameters are found to be 1.2 eV when both holes are in the p_{cc} bonding like orbitals, and 3.0 eV when either one or both of the holes are in the s or p_{cw} type orbitals.

The parameter U_0 allows for a direct energy shift of each component of the Auger line shape. It corresponds to the average hole-hole repulsion when the holes are delocalized about the complete system; hence the symbol U_0 . It is appropriate for molecules when partial localization of the final state holes is a "fait accompli", since the holes cannot get off the finite sized molecules (12). In extended covalent solids, these parameters have been found to become zero, as expected, since the two holes can now delocalize about the complete solid.

We conclude that U_0 and $U(\text{VBM VBM})$ are closely related, indeed essentially the same, and we shall use these terms interchangeably. This identity arises for two reasons. The effects of the "Cini-Sawatzky" distortion are to shift intensity downward away from the VBM, and for sufficiently large ΔU actually to shift it below the bottom of the valence band. Thus very small distortions occur, if at all, near the VBM. Further both $U(\text{VBM VBM})$ and U_0 reflect the delocalized hole-hole repulsion, i.e., when the holes are delocalized about the entire molecule, as described above. Thus, U_0 should be very small or near zero if the Cini-Sawatzky model is valid for PE.

In a study of the KVV AES spectrum of polyethylene (PE), Rye concluded that $U(\text{VBM VBM}) (= U_0)$ is about 10 eV (8), based upon his estimates of the energies of the VB, C 1s, and X-ray excited KVV features. Consistent with the above, he further suggested that the PE line shape and energy cannot be described consistently within the Cini-Sawatzky model. In contrast, we (14) found in previous work that the PE line shape and energy were consistent with the

Cini-Sawatzky model and that the values of ΔU are only about 1-3 eV depending on the orbital nature, and that U_0 is very small or zero.

The reason for these widely different conclusions is straightforward and unfortunately all too commonplace, namely different choices for referencing the relevant transitions (i.e., there were large variations in the absolute energy scale of the Auger line shape). However, the questions raised are very important and fundamental. Does the Cini-Sawatzky model adequately describe the Auger spectrum (line shape and energy) for PE?

Rye based his estimate of $U(\text{VBM VBM}) (= U_0)$ from X-ray excited KVV and core level values based on the following equation (15),

$$U_0 = E_{\text{a}}(\text{cvv}) + E_{\text{a}}(\text{c}) - h\nu - 2E_{\text{a}}(\text{v}). \quad (2)$$

Here $E_{\text{a}}(\text{cvv})$ is the observed energy of the CVV Auger transition on the binding energy scale. This approach has the advantage that the energy determinations are made with the same instrument using the same energy scale, and since two E_{a} terms enter with a positive sign and two with a negative sign, the effect of sample charging is presumably eliminated. We previously based our energy referencing on data in the literature. Therefore, we had no control over the energy calibration (14). The much better energy referencing approach of Rye suggested that the Cini-Sawatzky model for some reason is totally inadequate for PE.

In this study we have obtained new experimental XPS and AES data on PE samples from three sources. Experimental attempts to reduce charging in some instances were carried out; in other instances the effects of charging were presumably removed by proper determination of the energy scale. The Rye method to estimate

$E_{\infty}(cvv)$ and $E_{\infty}(v)$ in eq. (2) will be illustrated and a new and better method to find U_0 will be described. A small breakdown of the Cini-Savatzky model for PE is suggested from these determinations, but it is much smaller than the value proposed by Rye. Also, a possible differential charging effect is suggested for PE; this can have implications for the use of the Auger Parameter in some cases.

EXPERIMENTAL.

Polyethylene samples. Three different sources of PE were used in this study. Two PE sheets, one high density (HDPE) and the other low density (LDPE), were given to us by R. Rye. It was found that small pieces of the HDPE sample could be fractured at near liquid nitrogen temperatures to produce a clean surface. The LDPE samples were cleaned with acetone or HF. The results from only those surfaces where the XPS estimate of oxygen was less than 3% will be considered for energy reference purposes. The PE surface that was initially formed and exposed to the atmosphere was found to have relatively larger amounts of oxygen. A second set of high density PE samples was supplied by F. Campbell of the Naval Research Laboratory. These specimens were cast from HDPE beads that had no added anti-oxidants. Again either fracture surfaces or the cast surfaces were used with the criteria given above. A third series of experiments was made with a low density PE sample given to us by R. Baier of the State University of New York at Buffalo. This specimen was a thin sleeve that had been autoclaved and subsequently sealed before shipment to us. The inner surface from

small portions of the sample was used. The analyzed surface was in contact with itself by folding during storage.

Data collection. All spectra were obtained with a Surface Science Instruments SSX-100-03 X-ray Photoelectron Spectrometer operating at pressures in the mid 10^{-9} torr region or lower. This spectrometer uses a monochromatic Al K_{α} source. The VB, C 1s, and C KVV data were obtained after a wide scan spectrum was taken to check for surface contaminants. For some spectra an electron flood gun was used to reduce the effects of charging, and during the course of this study a gold screen was used over some of the samples (16). The spectra were recorded with the computer supplied with the spectrometer. Further data reduction and display were performed off-line.

Energy Referencing Procedures. The two energy calibration procedures, namely the Rye method (giving $U_0(Rye)$) and our modification (giving $U_0(Mod)$) are illustrated in Figs. 1 and 2 with data from a typical experiment. Fig. 1 contains a valence band XPS spectrum on the "experimental" binding energy scale as recorded by the instrument. Fig. 2 contains the as recorded Auger signal on a two-hole binding energy scale, $E_{\infty}(v) + E_{\infty}(v') + U_0$, which according to eq. 2 is equal to $E_{\infty}(cvv) + E_{\infty}(c) - h\nu$. The binding energy, $E_{\infty}(c)$, of the C 1s peak maximum is determined directly from the spectrum in that region. Thus $E_{\infty}(cvv)$, $E_{\infty}(c)$, and the VB spectra all are referenced to the same experimental energy scale. However, any shifts from sample charging or other errors in energy referencing are not removed by this procedure, rather the VB and Auger spectra simply have been placed on the same energy scale.

In the Rye approach for determining U_0 , the VB maximum (VBM) and Auger edge ($2 \text{ VBM} + U_0$) are estimated by the intersection point of a "tangent" line drawn along the edge of the lowest energy feature (the solid lines in Figs. 1 and 2) with the base line (usually found by the line through the points beyond the edge). The success of this method depends on whether the extrapolations to zero accurately locate the same edge, i.e., whether the two extrapolations are indeed related by VBM and $2 \text{ VBM} + U_0$. The intersection point was estimated to be at a binding energy of -0.8 eV in the VB spectra, Fig. 1, and at 3.6 eV in the Auger spectrum of Fig. 2 as pictured. Whether these intersections are relative to the Fermi level, vacuum level, or another arbitrary point is irrelevant, as long as the two intersection points are related as described above. The estimate of U_0 by this method is then 5.2 eV for the data in Fig. 1.

We note that the above procedure uses only $3\text{--}5 \text{ eV}$ of the VB and AES spectra near the edge for determining VBM and $2 \text{ VBM} + U_0$. We would like to utilize much more of the spectrum for energy referencing. Our approach uses a "model" VB and AES line shape that can be compared and matched with a much larger part of the experimental spectrum, and, thus, significantly increases the precision in determining these or similar reference points.

In Fig. 1, we use the X-ray excited VB spectrum obtained by Delhalle, et al., (17) as the model VB line shape (the dashed line in Figure 1) and a theoretical Auger line shape (the dashed line in Figure 2) obtained in our previous work as the model AES line shape. As stated above, a critical requirement is that these two

model line shapes be referenced to the same reference point exactly, which of course can be easily accomplished within the theory. In Figs. 1 and 2, the reference point is the nominal Fermi level as indicated by Delhalle, et al., (17) in the VB XPS spectra. Again, it makes no difference if this is correct or not, since the same reference point is used in the two model spectra.

In Figs. 1 and 2 the model line shapes have been optimally aligned with the experimental spectra. The shift, δ_m , of the VB model line shape with the experimental data in this case is -3.6 eV . The shift between the AES model line shape, $2 \delta_m + U_0$, and the experimental data is 4.5 eV in Fig. 2. By this approach the estimate of U_0 is 2.7 eV in this experiment.

The effects of redistributed primary and secondary electrons have not been corrected in the experimental VB and CVV spectra in Figs. 1 and 2. Thus, the model line shapes do not agree with the experimental spectra beyond about 20 eV below the edge. Nevertheless, we have increased the energy range used in our referencing method from the $3\text{--}5 \text{ eV}$ range to about 20 eV .

Determination of model line shapes. The critical point in determination of the VB and AES model line shapes is that they have exactly the same reference point. Consequently, it is difficult, if not impossible, to utilize purely experimental line shapes for both. We have the following choices. 1) An experimental Auger spectrum is used as a model to generate a semi-empirical VB model line shape that is automatically on the same energy scale. This is generally not done; although it indeed has been previously reported by self-deconvolution procedures (18). 2) A theoretical DOS is

used to generate both of the model line shapes using the appropriate matrix elements to weight the individual s, p, and d components of the DOS. For example, Sherwood has employed x-alpha muffin-tin calculations to several systems with good agreement between X-ray induced experimental VB data and computed spectra (19). 3) An experimental VB spectrum is employed to generate a semi-empirical Auger model line shape that automatically has the same reference points. The latter two choices are equally plausible. Since we have previously reported the PE Auger line shape generated semi-empirically from the VB XPS spectrum of Delhalle, et al., (17) this was the obvious choice for this study. For details of the procedure we used to find the model line shape, see the appendix. It should be noted that the second approach indicated above would be best if the reference point is to be located at the theoretical Fermi level, but this is not necessary to determine U_0 .

RESULTS AND DISCUSSION

Fig. 3 summarizes the results for the 23 measurements made with the samples from three different sources utilizing different charge reduction techniques. The results are plotted versus $d_{H'}$, the energy shift required to obtain optimal alignment between the model VB Delhalle line shape and the experimental VB spectrum. This parameter can be viewed as the nominal charging shift assuming no charging effect in the Delhalle data. Several important points are evident from this data.

Experimental and Calibration Techniques. Most evident in the data is the significantly increased precision obtained with our modified technique. In spite of the significant variation in charging, we are able to obtain the C 1s XPS binding energy (found at 277.35 eV relative to Dehalle's Fermi level) to within a 1 eV variation. Likewise the variation in U_0 found by our method is much smaller than that from the approach by Rye (8). Whereas our estimates of $U_0(\text{Mod})$ vary over a 2 eV range, the variation in $U_0(\text{Rye})$ varies over a range of 15 eV. This is due, in part, to the use of much more of the spectral region with our modified technique. Although our approach requires a much greater effort to obtain the line shape, there can be no doubt that it dramatically increases the precision, and thus for some applications it is well worth the effort.

Determination of U_0 . The average value of $U_0(\text{Rye})$ is 4.6 ± 2.5 eV while that for $U_0(\text{Mod})$ is 1.9 ± 0.6 eV. This can be compared to the single result of 10 eV obtained by Rye (8); a factor of two larger than our average $U_0(\text{Rye})$, but still within our range of estimates for $U_0(\text{Rye})$.

Although there is some overlap in the two average ranges, we conclude that there is a systematic difference between the average values of $U_0(\text{Rye})$ and $U_0(\text{Mod})$, and that the Rye approach over-estimates the hole-hole repulsion parameter. This occurs because the fold of a function increases from the edge much more slowly with energy than the original function. Fig. 4 illustrates this by showing a simple trigonometric DOS, namely N and the self-fold, $N+N$, of this DOS. The tangent line is uniquely defined

for N and intersects the base line at zero binding energy, which we will call the VBM. We illustrate two possible tangent lines to the N_{1s} function, one with the same slope as for N that intersects the baseline around 7 eV, and one with significantly lower slope intersecting around 3 eV below the Fermi level. We conclude that the extrapolation to zero in the Auger spectrum generally occurs at an energy much further from the reference point than in the VB spectrum. This gives an over-estimate of the value $2 \text{ VBM} + U_0$ relative to VBM. We conclude that the simple extrapolation at the edges is not adequate to find U_0 , because the intersection points obtained from the extrapolations are not, in fact, quantitatively related, a critical requirement of the method.

It should be pointed out also that in Rye's study, a non-monochromatic Mg K_α X-ray source was used. With PE there is a small satellite contribution (due to the K_{α1} X-ray radiation from Mg and also present with Al) of the VB peaks in the 10-15 eV region that falls near the edge of the VB spectrum. This is in the region used to estimate E_v (v) in the Rye method. The magnitude of these satellite contributions, while small, could add to the uncertainty in the estimate of VBM by the simple extrapolation approach. Such satellites are not present in our data, since a monochromatic Al K_α source was used.

The average $U_0(\text{Mod})$ of 1.9 ± 0.6 eV, or the value at zero charging, 2.2 eV, indicates a small break down in the Cini-Sawatzky expression for PE, that suggested U_0 should be zero (9-11). U_0 is much smaller however than the 10 eV found by Rye. If Rye's conclusion were correct, PE would exhibit a small (1-3 eV) ΔU

correlation parameter and a very large (about 10 eV) U_0 shift parameter. This would be difficult to understand. On the other hand, since U_0 indeed is small (1-3 eV) as indicated by our $U_0(\text{Mod})$, two explanations might be possible. First, one might be able to explain the line shape shift to higher binding energy simply by increasing ΔU , since this distorts the line shape in the right direction. However, we find that this distortion makes the theoretical lines shape deviate significantly from the experimental spectral line shape, and hence this most straightforward explanation is invalid. We suggest the non-zero U_0 may arise because of the limited one-dimensional hopping route for delocalization. Indeed, it has already been reported that the Cini-Sawatzky theory may not be valid for one-dimensional chains and perhaps even in two-dimensional systems because of the limited number of delocalization paths (11,20).

The Cini-Sawatzky expression was derived for metals where $\Delta U = U_{11}$ (the single site hole-hole repulsion) and U_0 is definitely equal to zero because of the short screening lengths in metals. In a series of papers [12-15], we modified the Cini-Sawatzky expression slightly by introducing two parameters $\Delta U = U_{11} - U_{12}$ and U_0 , and found that we could adequately interpret the Auger spectrum for several alkanes and alkenes, graphite, diamond, and other covalent systems. However, this modified expression apparently does not work for PE, because it predicts that U_0 should be zero for an infinitely long chain, and now we find that it is not. That the modified expression does not straight-forwardly work for PE suggests that similar problems also exists for the one-dimensional

chains and rings of the alkanes and alkenes. This was not evident for the molecules because U_b is non-zero in any event.

Our problem with PE suggests that a more basic theory must be developed for covalently bonded systems. In the absence of such a theory, the Cini-Sawatzky expression will continue to be utilized, but one must realize the parameter U_b accounts for some errors in the Cini-Sawatzky expression for covalent systems, which assumes an infinitely fast hopping rate. We prefer to think of U_b as the "effective" hole-hole repulsion at times shortly after the Auger decay (i.e., on the scale of time less than it takes for the Auger electron to escape). The U_b found for PE is about the same as that found for benzene and cyclohexane, suggesting that the "delocalization length" in times short compared with escape of the Auger electron is about five or six carbon atoms. At longer times the holes will delocalize further along the chain and the effective hole-hole repulsion is expected to go to zero.

The Effects of Charging. Even with our dramatically increased precision, we still cannot detect significant trends between the different samples, but a dependence on the experimental techniques is clear. With the LDPE samples from R. Baier and the HDPE specimens from F. Campbell, the charging shifts with the flood gun on were about 0 to -1 compared with 3 to 4 eV, with the flood gun off (see Fig. 3). Wider variations in δ_w were found with the samples provided by R. Rye with or without the use of the flood gun. No definite trend in δ_w was found with the latter set of samples, and the reason for the larger variation is not clear. One possibility is that the Rye samples were somewhat larger, and this

could have led to somewhat poorer electrical contact with the sample holder compared to the work with the other specimens.

Fig. 3 also shows a systematic linear decrease in $U_b(\text{Mod})$ with increased charging. This also may be present in $U_b(\text{Rye})$, but the scatter of data does not make this evident. We suggest this linear decrease may arise from differential charging at the surface. Such differential charging shifts have been suggested previously (21).

On the binding energy scale in this study, the VB, 1s, and Auger transitions are at 0, 285, and 1210 eV, or electron kinetic energies at 1480, 1195, and 270 eV, respectively. The mean free paths of electrons at these kinetic energies are around 4.7, 4.2, and 2.0 nm, respectively (22). Thus the Auger electrons have a shorter escape depth than the VB and core electrons. If the potential drop due to charging extends over more than 2nm from the surface, the Auger electrons will experience a smaller charging shift ($\delta(2\text{nm})$) on average than the VB and core electrons ($\delta(4.5\text{nm})$). From eq(2), we then have $U_{\text{chg}} = U_{\text{core}} + \delta(2\text{nm}) - \delta(4.5\text{nm})$, the difference, $\delta(2\text{nm}) - \delta(4.5\text{nm})$, increasing with δ_w . We believe this is causing the negative slope of 0.17 in the $U_b(\text{Mod})$ curve in Fig. 2. Although not visible from Fig. 2, the $E_k(1s)$ also has a very small negative slope (-0.03) consistent with a smaller differential charging shift expected in this case because of the smaller (300 eV) energy difference with the valence band electrons.

The above interpretation indicates that all effects of charging on the experimental spectra may not be removed by our referencing technique. The Auger parameter has been used by many

in recent years to eliminate the effects of charging shifts with X-ray excited spectra. Indeed this was one of the purposes for its definition (5). The Auger parameter, α , is defined

$$\begin{aligned}\alpha &= E_{\text{a}}(\text{jkl}) - E_{\text{a}}(\text{j}) + h\nu \\ &= E_{\text{a}}(\text{j}) - E_{\text{a}}(\text{jkl}) + h\nu\end{aligned}\quad (3)$$

where the Auger electron energy, $E_{\text{a}}(\text{jkl})$, and core electron energy, $E_{\text{a}}(\text{j})$, are defined on the binding energy scale. In instances where there is a large difference between $E_{\text{a}}(\text{jkl})$ and $E_{\text{a}}(\text{j})$ and one of the transitions has a relatively low value (probably <400 eV), the value of the Auger parameter may be affected by charging. Additional studies are needed to confirm if this is a truly general effect.

Sample alteration. There were some differences in the VB spectra between the LDPE and HDPE samples. With the LDPE samples, another peak between the main lines (about 9 and 15 eV in Fig. 1) was present. This feature was of equal, or greater, intensity than the other two main peaks. Also, its intensity appeared to increase with time of exposure to the X-ray beam sometimes. The feature was found with or without the flood gun in operation.

This additional feature is similar to peaks observed with some cycloalkanes (C_1 , C_7 , and C_9) and is believed to arise from topological features in amorphous materials (23). It is possible that this feature may be due to fragmentation of the LDPE chains. LDPE has a small number of methyl groups that are attached to the main PE backbone. With HDPE the number of such methyl groups is much smaller. The pendent methyl groups may serve as active sites for fragmentation or cross-linking.

SUMMARY

In summary, we have made the following conclusions:

1. A method to determine U_0 has been developed that gives much more precise and accurate values than the simple extrapolation technique.
2. A breakdown in the Cini-Sawatzky expression, as modified for covalent systems, has been observed. This may result from the longer one-dimensional delocalization times required in long chain polymers. Although U_0 is finite, it is much smaller than previously suggested by Rye; this allows for the reasonable explanation involving delocalization times in one-dimensional systems.
3. We believe we have observed a differential charging effect in the spectra. This effect also may mean that the Auger parameter may not eliminate all effects of charging. More study is needed to confirm this suggestion.

APPENDIX

Model Auger line shape. The Cini-Sawatzky theory has been the basis for interpretation of Auger line shapes for several years. It has been used to gain a greater understanding of bonding in a wide variety of systems, including metals, alloys, insulators, and molecules. This work has been reviewed elsewhere (6). The Auger line shape required for comparison with experiment in our method of determining U was generated by the following equation (6),

$$I_{\text{kw}}(E) = B \Sigma_{\text{w}} [P_{\text{kw}} R_{\text{w}} A(E + U_{0,\text{w}}) \Delta U_{\text{w}} \rho_{\text{w}}] \quad (\text{A1})$$

In eq. A1, A is the Cini-Savatzky function (9-11),

$$A(E, \Delta U, \rho, \rho') = \frac{\rho^* \rho'(E)}{[1 - \Delta U I(E)]^2 + [\Delta U \pi \rho^* \rho'(E)]^2} \quad (A2)$$

which introduces hole-hole correlation effects, and distorts the DOS self-fold. $\rho^* \rho'(E)$, is obtained from the proper weighting of the s and p components in the VB spectrum obtained from Delhalle, et al., (17),. Thus the self-fold of ρ guarantees that the VB and theoretical Auger line shapes have a common reference point. ΔU is the effective hole-hole correlation parameter and, $I(E)$ is the Hilbert transform,

$$I(E) = \int \rho^* \rho(\epsilon) / (E - \epsilon) \, d\epsilon. \quad (A3)$$

Additional arguments have been included in A to note that the total theoretical kvv line shape is a sum of components, with each 11' component (e.g., the ss, sp, and pp components) having an energy shift, $U_{0,r}$, and a hole-hole correlation parameter, $\Delta U'_{r'}$, and with each component derived from a fold of the l and l' DOS (e.g., s or p). B is a normalization constant, and the R_i 's are core hole screening factors. Further details of this approach have been given elsewhere (6).

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Figures

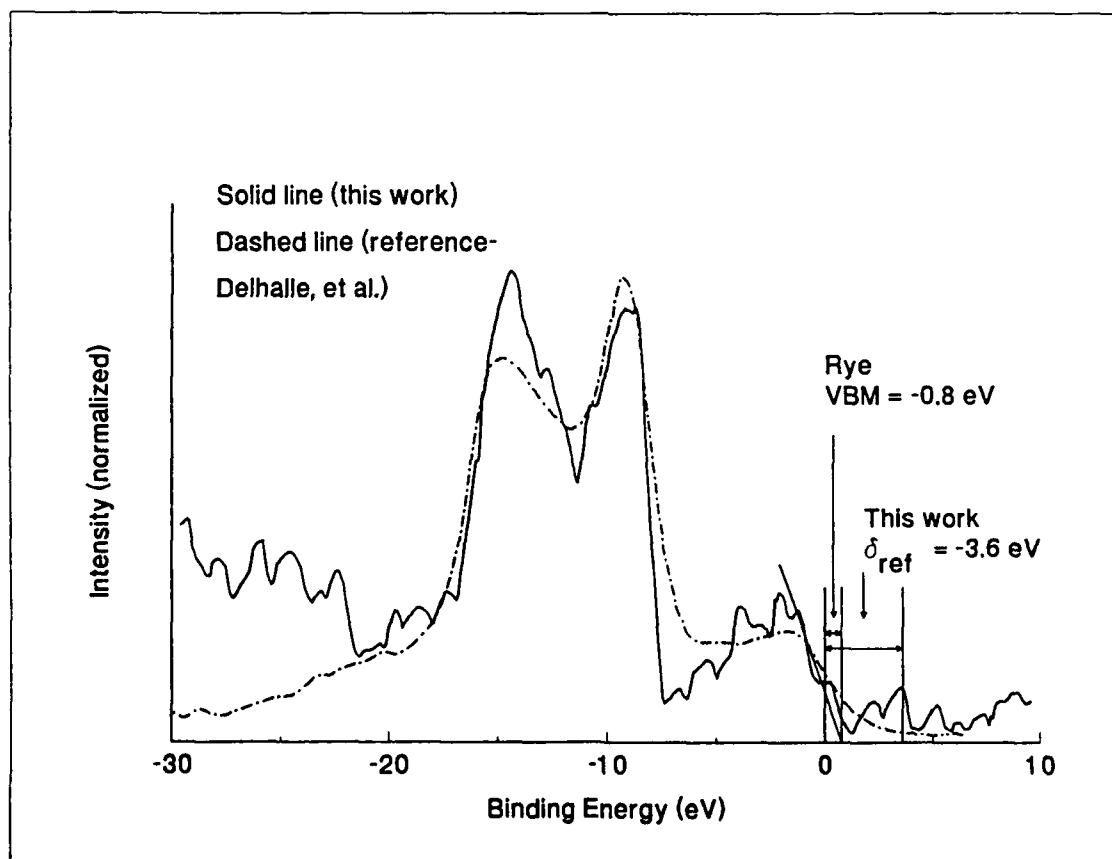
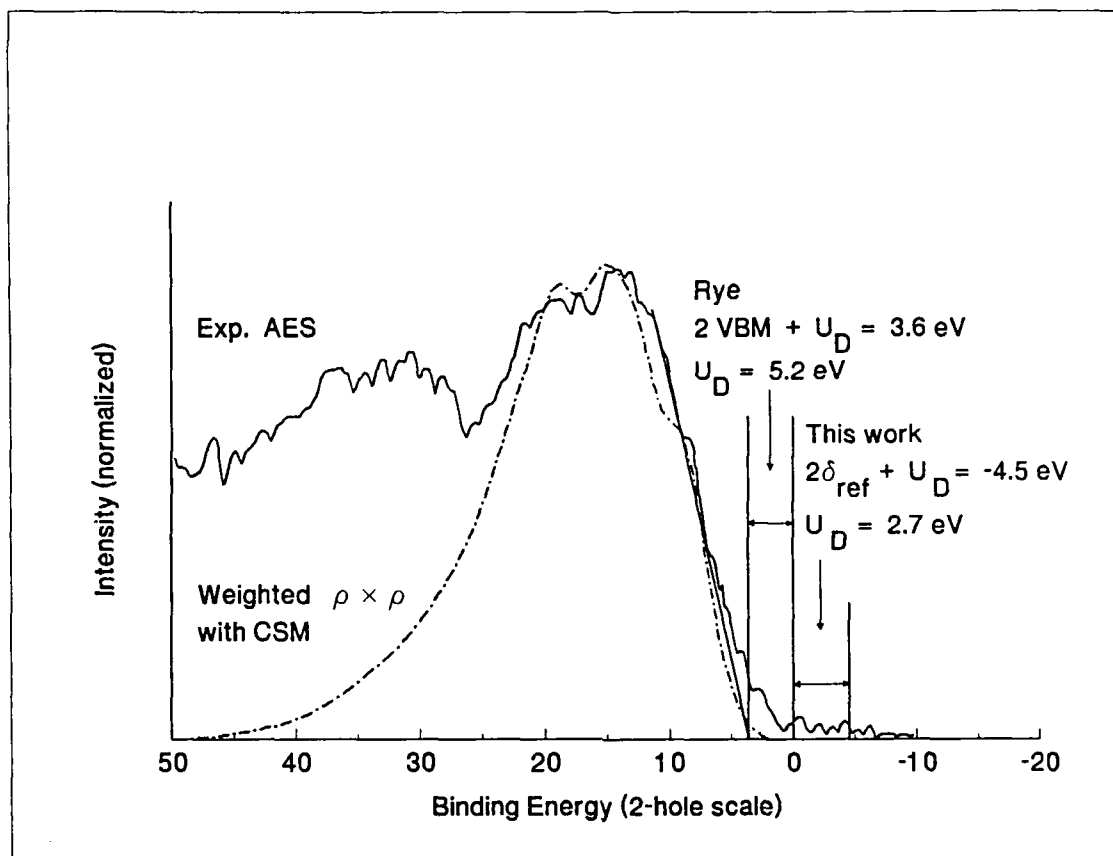
1. A comparison is shown of the experimental VB spectrum from high density PE with the model spectrum obtained from Delhalle, et al. (17). The model spectrum has been aligned (requiring a shift of -3.6 eV) and normalized to the experimental spectrum. The Rye approach and our modified approach for locating the valence band maximum (VBM) and reference point are illustrated (see text).

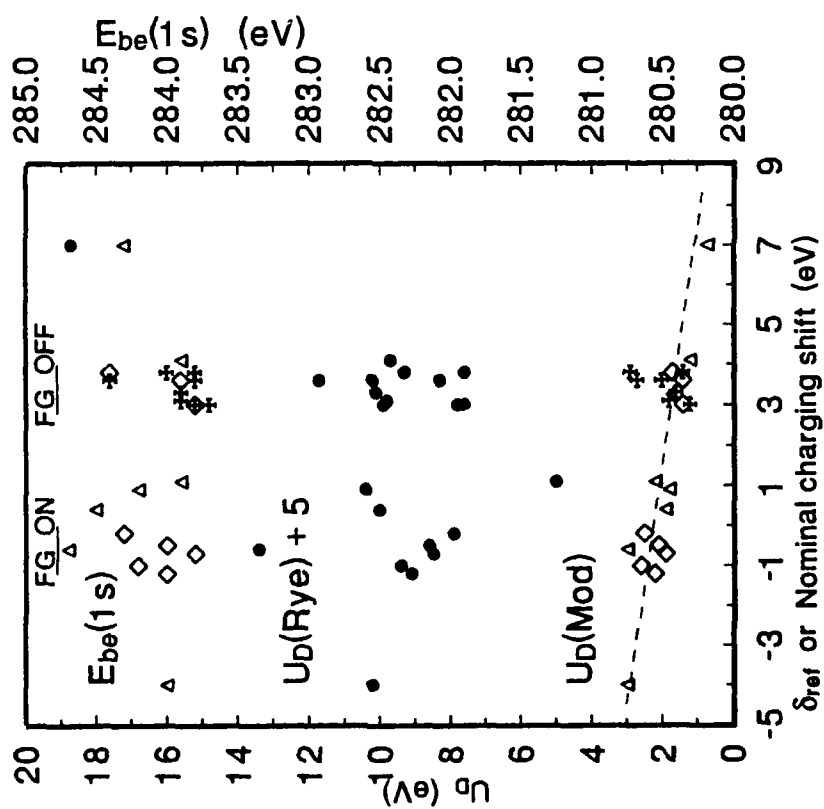
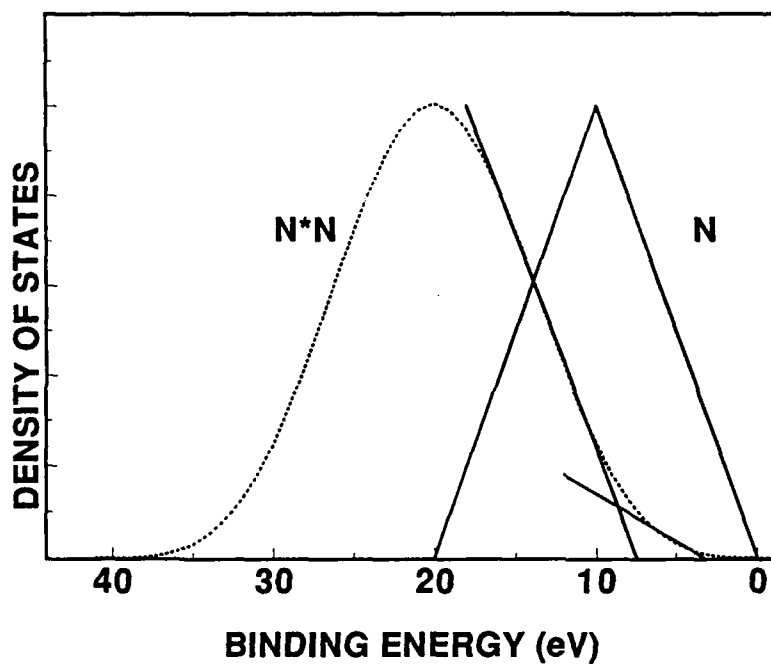
2. A comparison is presented of the experimental CVV spectrum from the same experiment as that in Figure 1 for high density PE with the model line shape generated as described in the text. The model spectrum has been aligned (requiring a shift of -4.5 eV) and normalized to the experimental spectrum. The energy is plotted on the two hole binding energy scale. The Rye and modified approaches for locating the VBM and reference points are illustrated (see text).

3. The 1s binding energies (E_{1s}), and U_b values obtained utilizing the Rye extrapolation approach, $U_b(\text{Rye})$, and our modified approach, $U_b(\text{Mod})$, are plotted against the shift in VB spectra from the model spectrum (δ_{M}) for the 23 different measurements made in this work. δ_{M} is nominally equal to the charging shift. A linear regression line is shown for the $U_b(\text{Mod})$ values revealing a negative slope to these data (see text). The open triangles indicate data on the Rye samples with and without a flood gun. The diamonds and the crosses show data with the Baier and Campbell samples,

respectively. All of the $U_b(\text{Rye})$ values are indicated by closed circles. Except for the Rye samples, the data fall between about 0 and -1.2 eV charging shift when a flood gun was used to reduce charging, and between 3 and 4 eV charging shift when the flood gun was off.

4. A plot of a triangular DOS, N , and its self-fold, $N*N$ is shown. The triangular DOS has $\text{VBM} = 0$. Two reasonable tangents to the $N*N$ curve are drawn, one with the same slope as for N , and one with much lower slope. These tangents intersect the base line at 3-7 eV below the zero point. A tangent intersecting at zero binding energy would have a very low slope, and would not normally be drawn. This illustrates that the Auger tangents do not intersect at $2*\text{VBM} = 0$; and hence in this case the Rye procedure overestimates U_b by 3-7 eV.





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